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POSSIBILITY OF A REAL DEVIATION FROM FARADAY'S LAW OF ELECTROLYSIS

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It has been observed by the author (Palit 1962a, b, 1963) that at a fixed voltage the current changes considerably on making the electrolyte flow past the electrodes, particularly so, if the electrolute is a weak conductor. It appears that some conducting zone which probably is of different structure from the main bulk of the solution forms near the electrodes. Since structure pomotes electronic conduction it was considered of interest to check the possibility of existence of non-electrolytic conduction in such weakly conducting systems. This was considered more worthwhile by the fact that practically all checks on Faraday's law have been carried out with fairly conducting electrolytes and no work appears to have been done with poor conductors, say, water itself. Our results throw considerable doubt on the validity of Faraday's law in such systems.

The experimental set-up is a very simple one, consisting of a beaker with two platinum wire electrodes inserted from the bottom. Two (or more) such are connected in series, one containing freshly distilled conductivity water and another containing a 0.5 N potassium sulphate solution serving as a coulometer (Abresh *et al.* 1960). The evolved gas a is collected in graduated test tubes inverted over the electrodes. About 20 to 30 milliampere D.C. current is sent through the system for a couple of hours or so to pre-saturate the electrolytes with hydrogen and oxygen. Electrolysis is now allowed to occur with 50 to 100 microampere current for three to five days or more until a few cc (usually 3 to 5 cc) of gas collects in the coulometer. The results are most unexpected.

If Faraday's law holds good, it is expected that equal volume of gas would collect in the two vessels. It is, however, observed (vide table) that the volume of gas collected over conductivity water at a particular electrode is much less than that collected over the coulometer at the same electrode. This occurs both at the anode and at the cathode. It was first thought that this may be due to the unequal solubility of the gas in the two electrolytes. To offset the effect of any such complicating factor, the electrolytes were not only presaturated with electrolytic gas by prolonged electrolysis as mentioned above, but the same sample of electrolyte was used in a number of consecutive experiments; this, however, made no difference in the results. Our observations can be summarised as follows.

(i) Wide deviation from Faraday's law is observed on electrolysis of conductivity water, provided the current is kept quite low say, of the order of a fraction of a milliampere or still lower.

(ii) The departure from Faraday's law tends to disappear with increasing concentration of electrolytes and somewhere in the range 0.01N to 0.1N the deviation becomes hardly detectable.

(iii) The lower the current and consequent less physical disturbance near the electrodes, the higher is the departure from Faraday's law.

More than a hundred experiments under varied conditions were made and they all confirmed the above results. The results were further confirmed by collecting electrolytic gas (hydrogen and oxygen together) in a closed apparatus similar to that recommended for use in coulometry (Abresh *et al.* 1960). The following is a typical set of results of one experiment with five cells and a coulometer in series.

TABLE

Electrolyte	Current milliamp	Volume of gas collected in the cell over cathode	Volume of gas collected in the coulometer in series over cathode	Per cent non-electrolytic conduction
Conductivity Water	0.100	0.6 cc	3.3	82%
N/10,000 K_2SO_4	0.100	1.8 cc	3.3	46%
N/1,000 K_2SO_4	0.100	2.4 cc	3.3	27%
N/100 K_2SO_4	0.100	3.1 cc	3.3	6%
N/10 K_2SO_4	0.100	3.3 cc	3.3	0%

It has not been possible to find any source of error in the above results and so it is concluded that Faraday's law is of limited validity in poorly conducting systems. An almost complete break-down of Faraday's law is easily observed by carrying out electrolysis of conductivity water in a closed system (Abresh, *et al.* 1960) using platinum electrodes (0.5×1 cm) and a current of 25 microamperes. It is observed that hardly any gas collects over even a couple of weeks whereas according to Faraday's law more than 6cc should have collected by this time; even in the coulometer in series only about a couple of cc gas collects. It appers that when there is paucity of ionic current carriers, the current tends to pass by some other mechanism, which is probably electronic.

There have been many reports in the literature (Hampel, 1964) about less than 100 percent current efficiency and these are generally explained as due to side reactions and and other causes. Non-electrolytic current conduction should now be included as one of the factors for lower than theoretical current efficiency. Whether the non-electrolytie passage of current is caused by electronic conduc-

tion, or by conduction by charged water molecules, or by some other mechanism is an open question and would be duly answered particularly by transference experiments now under way. Further work is in progress and detailed results will appear elsewhere.

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